Reduced Precious Metal Catalysts for Methane and NOx Emission Control of Natural Gas Vehicles

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ACE128

Overview

Timeline

- Start: May 1, 2018
- End: April 30, 2021
- 30% complete

Budget

- Total project funding
  - DOE: $2,000,000
  - UH & partners: $525,380
- Funding received
  - FY19: $660,176 (by 4/1/2019)

Barriers/Targets

- Replace/supplement diesel with domestic natural gas (NG) for transportation
- Methane is greenhouse gas (25x CO_2); CH_4 GHG emissions above the 30 mg/mi light- duty vehicle cap count against fuel economy
- U.S. EPA mandates tailpipe methane emissions at 0.1 g/bhp-h for heavy-duty vehicles (95% reduction) & NOx emissions at 0.2 g/bhp-h
- State-of-art three-way catalyst (TWC) ineffective for methane oxidation at < 400 ^oC

→ *Need for low cost emission catalyst for stoichiometric NG vehicles*

Partners

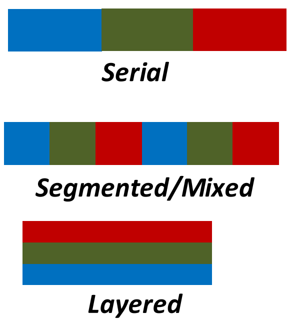
- U. Houston (lead)
- CDTi Advanced Materials, Inc.
- University of Virginia
- Oak Ridge National Lab

Project Premise and Hypothesis

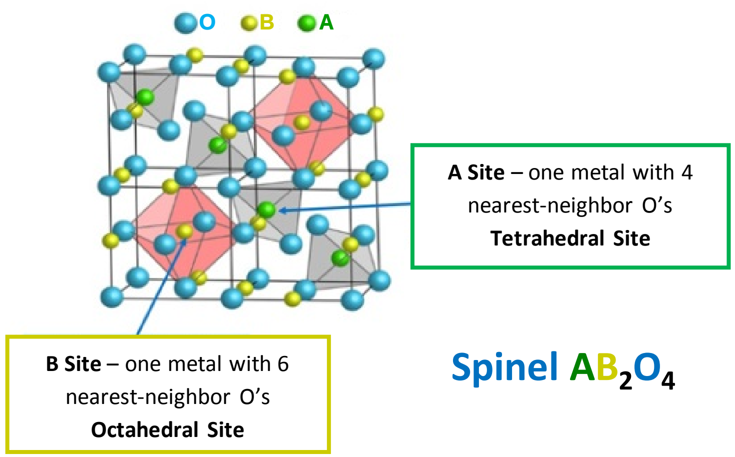
Develop the: ***FWC = Four Way Catalytic Converter***

to enable reduced emissions of CH_4 in addition to CO, NOx & NMHCs from CNG-fueled vehicles

Material	**M-OC**	+	**HC-OC**	+	**N-RC**	= ?
	AB_2O_4/Al_2O_3		**Pd + CeO_2/ZrO_2/Al_2O_3**		**Rh/Al_2O_3**	
Function(s)	**Methane oxidation**		**HC + CO oxidation**		**NO_x reduction**	
	…………Oxygen storage/release………					

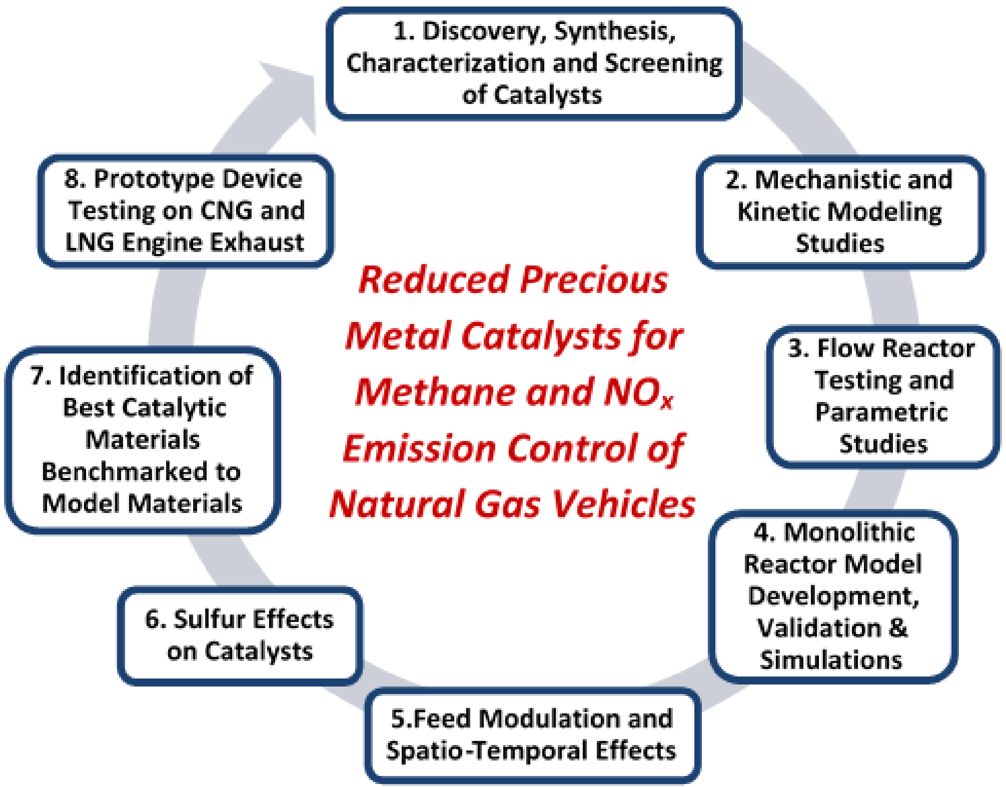


Spinel in combination with low levels of precious metals are cost-effective solution for coupled methane, CO and NO_x conversion in stoichiometric natural gas vehicle exhaust.



Spinel AB_2O_4

Project Approach and Collaborations



Comprehensive program spanning discovery, development, evaluation, and technology transfer will help to bring down cost barriers and accelerate the deployment of NG vehicles in the medium- and heavy-duty sectors

BP1 Milestones

Milestone	Description	Status
Material Discovery Complete	Identify at least one Spinel material using descriptor-based density functional theory (DFT).	Several Spinel materials have been evaluated and rank-ordered based on methane oxidation activity. DFT screening efforts are underway to compare with measurements.
Reference and Baseline material performance testing Complete	Document flow reactor performance testing of Reference and Baseline FWC materials in terms of methane, CO, and NO_x conversion.	Reference and Baseline catalysts have been evaluated for both steady state and modulation conditions.
Kinetic model tuning Complete	Develop, tune and validate monolith reactor model containing the global kinetics of the Baseline FWC material.	Experiments are underway to compare activities of different functions of the Baseline material comprising Spinel and precious group metal (PGM). Kinetics evaluations are underway as first step towards kinetic model development.
Identification of candidate material (Go/No Go)	At least one FWC material that lights off below 300 ^oC and has less than 30 g PGM/ft^3 at 50k h^{-1} space velocity (following USDRIVE specified protocol, if available) identified.	Several FWC materials comprising PGM top-layer and Spinel base-layer have demonstrated light-off at ~300 ^oC at 90 h^{-1} space velocity using realistic feed with PGM loading of 30 g/ft^3.

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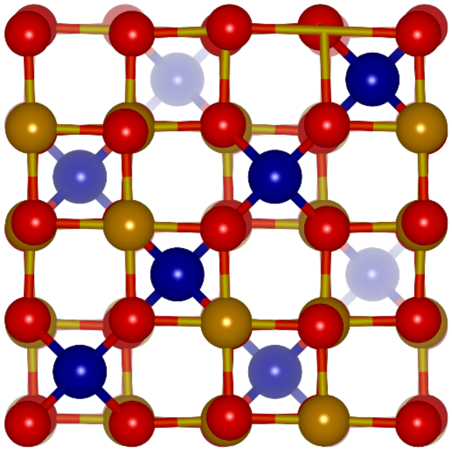
DFT Descriptors for CH_4 Conversion



Tetrahedral sites
Octahedral sites

Oxygen vacancy formation energy
- indicates lattice oxygen release/uptake

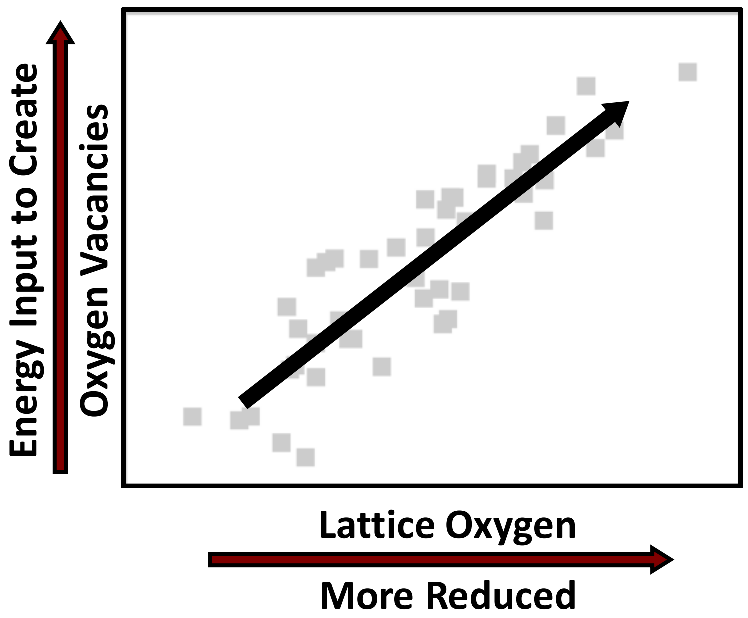
H-binding energy
- indicates C-H bond activation
  (a key step for hydrocarbon oxidation)

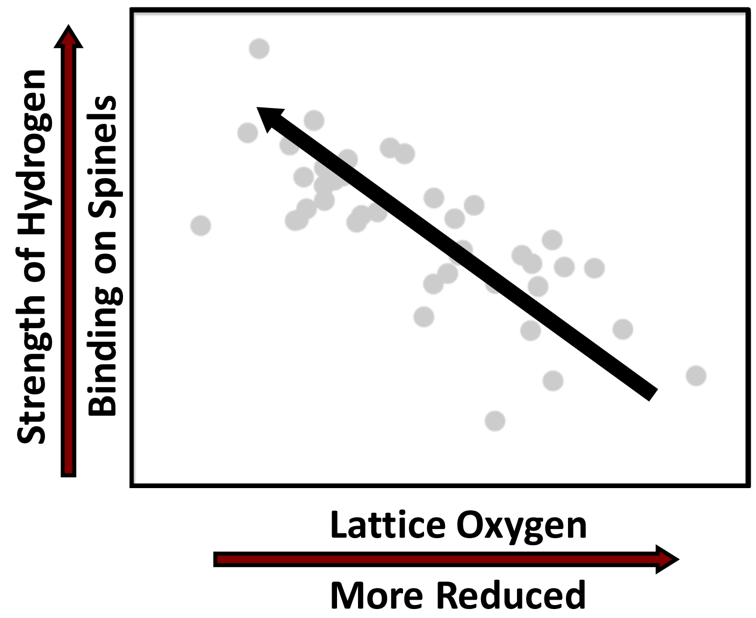
Both descriptors closely related to structure and composition of the Spinels, and can be used for performance screening

Structure - composition space of spinel oxides ($A_{1+x}B_{2-x}O_4$)

- Structural Phases: Normal; Semi-Inverse; Inverse
- Compositions: A, B = {Mn, Fe, Co, Ni}

Descriptor-based Spinel Screening





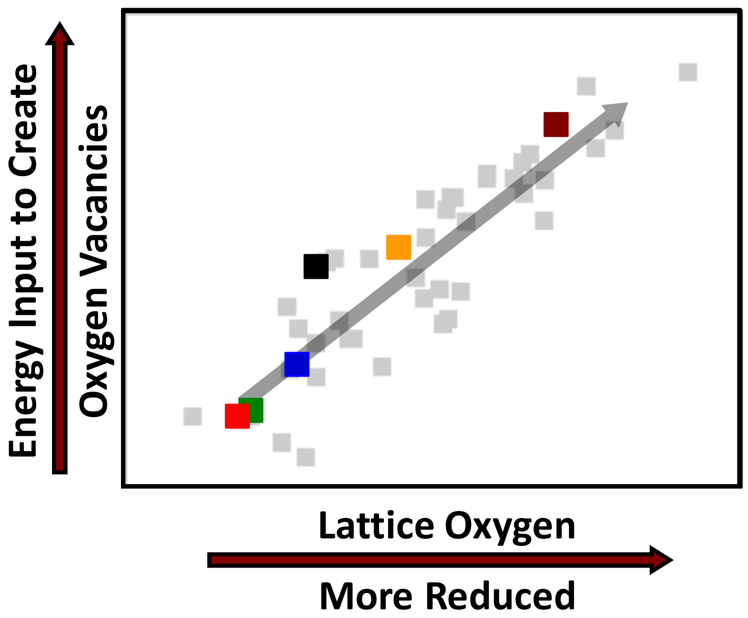
Oxygen vacancy formation energy

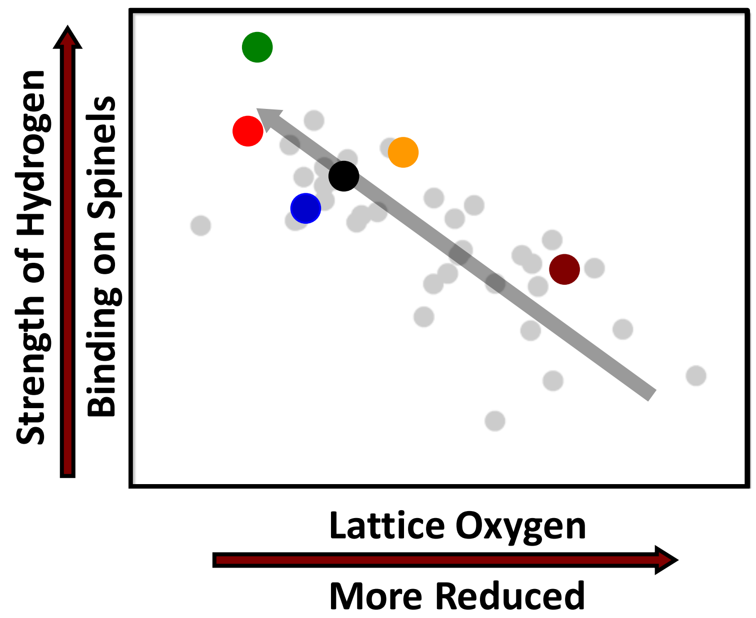
Higher energy required to create oxygen vacancies in materials with highly reduced lattice oxygen

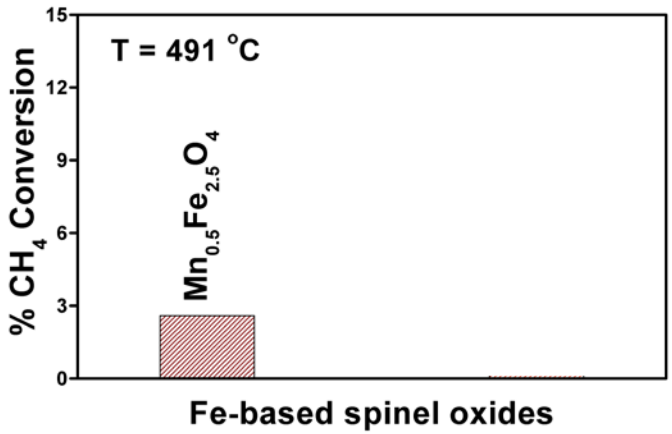
H-binding energy

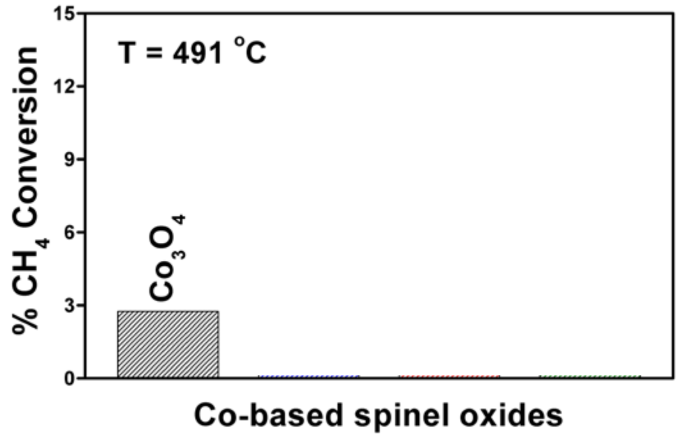
Stronger H-binding observed over materials with less reduced lattice oxygen

CH_4 Conversion Performance









Summary: Descriptor DFT

- DFT reliable for screening candidate Spinels
- Experimental trends along with DFT study portend need for:
  - Lower oxygen vacancy formation energies
    (marks low temperature vacancy creation)
  - Stronger H-binding
    (crucial for C-H bond activation – primary step for HC oxidation)

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Kinetics & Flow Reactor Studies

Baseline Catalyst: **30** g PGM/ft^3 — **100** g Spinel/L

"30/100" — 95% Pt, 5% Pd — $Mn_{0.5}Fe_{2.5}O_4$

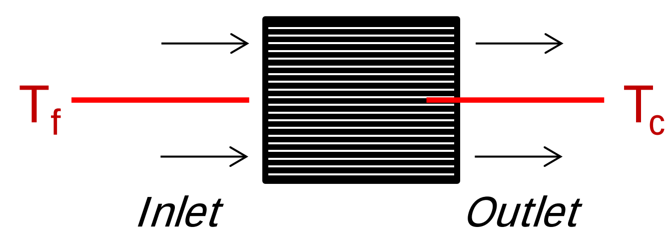
"Spinel": 25% Spinel, 75% γ-Al_2O_3

Feeds

	Steady	Modulated
	λ= 0.995	$\langle\lambda\rangle$ = 0.995 (0.981-1.009 @ 0.33 Hz)
CH_4	1500 ppm	1500 ppm
CO	8000 ppm	8000 ppm
H_2	2000 ppm	2000 ppm
NO	1000 ppm	1000 ppm
O_2	6700 ppm	4500 ppm (1.5 s) 8900 ppm (1.5 s)

* **Background**: 10% H_2O, 10% CO_2, bal. N_2

$$\lambda = \frac{0.5 \times [CO + 2{*}O_2 + NO + H_2O + 2{*}CO_2]}{[CO + CH_4 + CO_2] + 0.25 \times [2{*}H_2 + 4{*}CH_4 + 2{*}H_2O]}$$

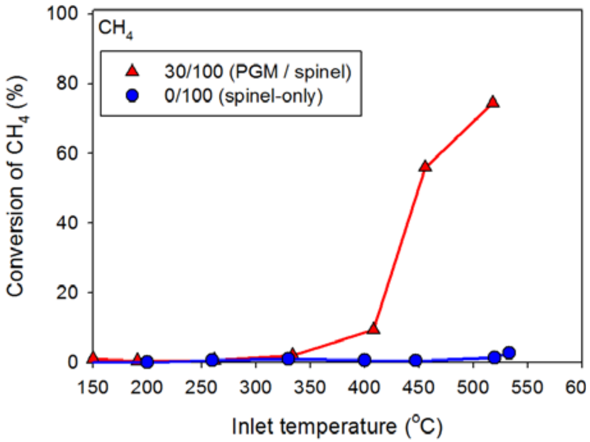


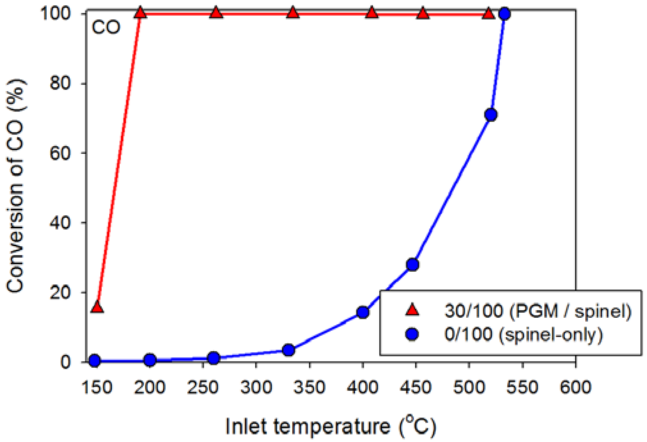
Monolith Catalyst
(1 x 0.84 in.)

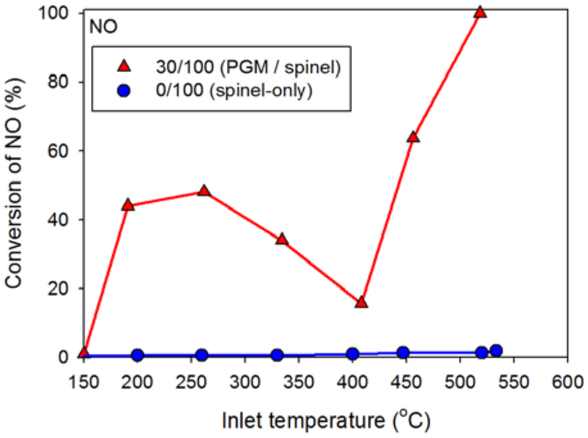
Baseline Catalyst: Impact of Ingredients

Baseline (CDTi) X/100
X = 0, 30 g PGM/ft^3, 100 g Spinel/L

GHSV = 40k hr^{-1}
Steady Feed
λ = 0.995







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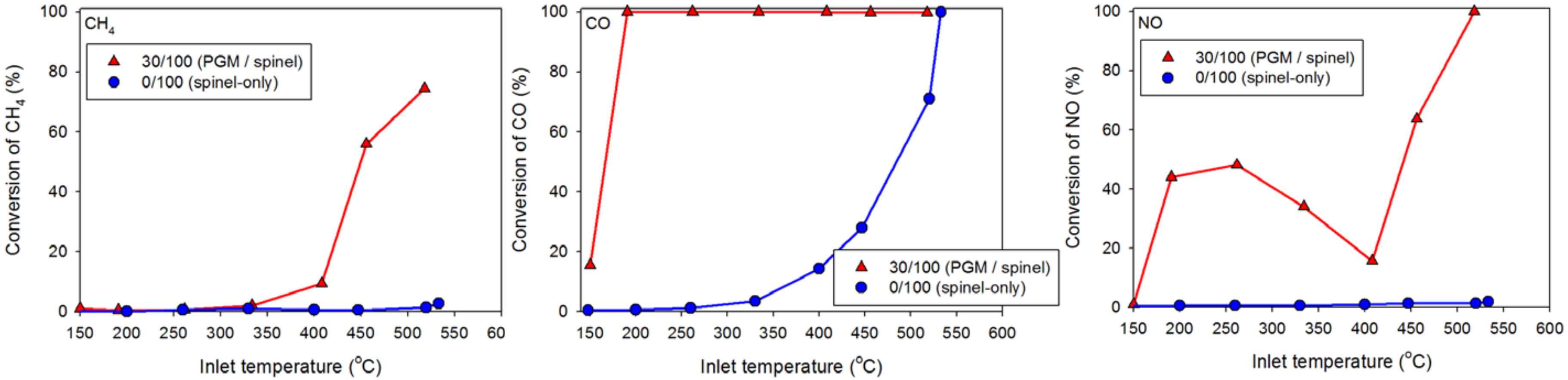
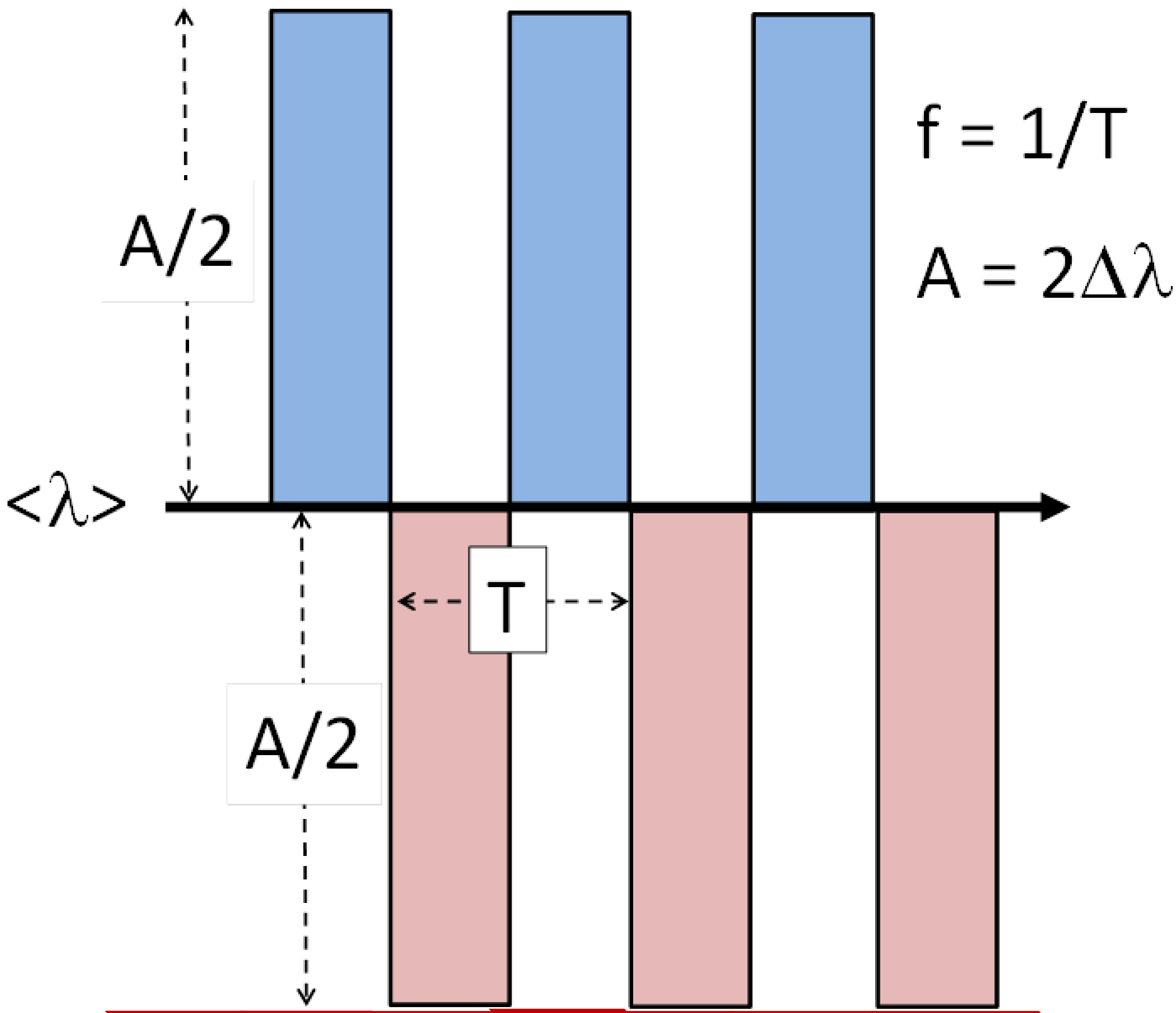


- *For steady feed, PGM is active component; $Mn_{0.5}Fe_{2.5}O_4$ Spinel is not*

Modulation

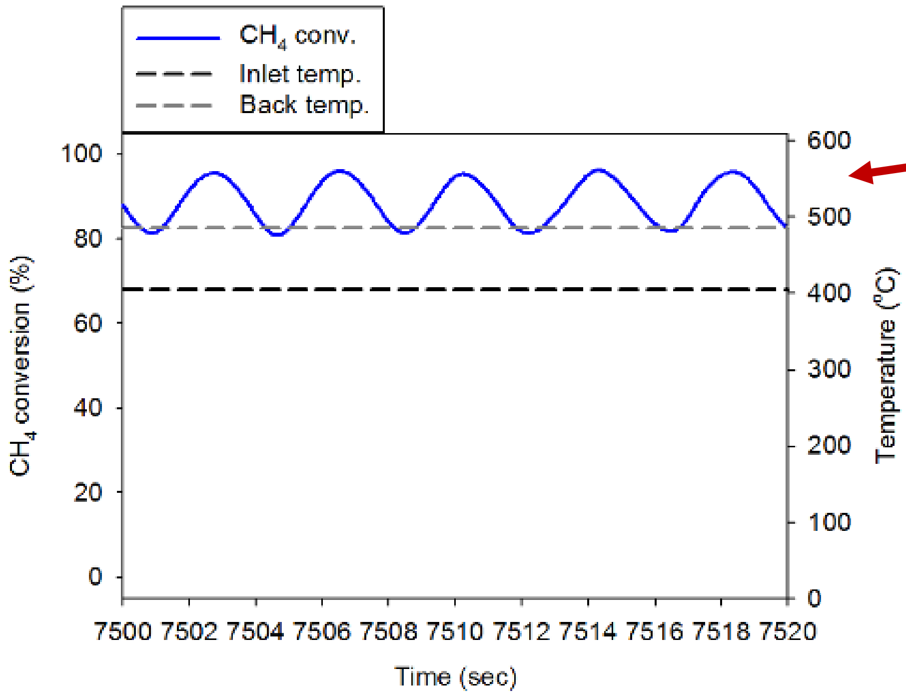


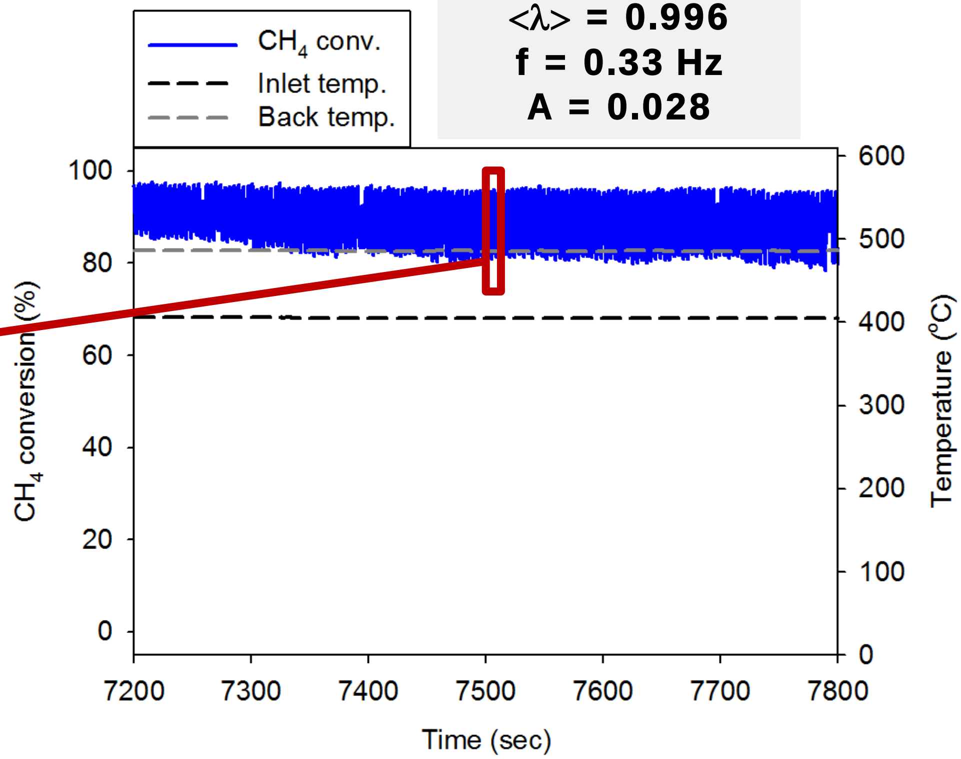
Modulation Impact

Baseline (CDTi) 30/100
30 g PGM/ft³, 100 g Spinel/L

[with O_2 modulation at 405 °C]

GHSV = 40k hr^{-1}
<λ> = 0.996
f = 0.33 Hz
A = 0.028

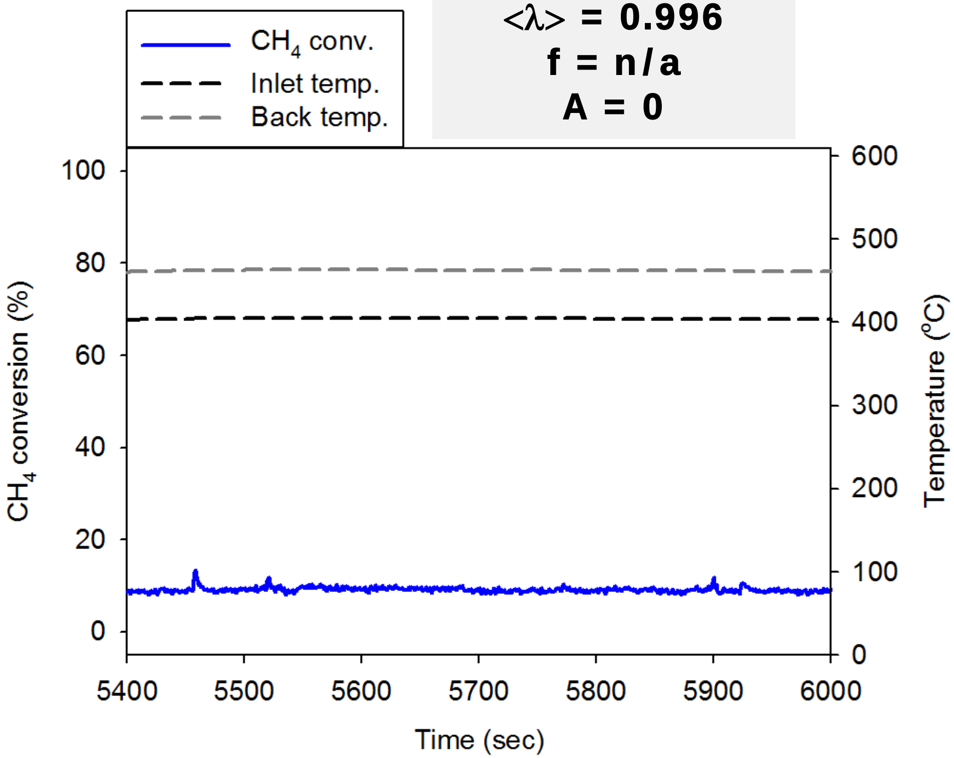




Modulation Impact

[w/o O_2 modulation at 405 ºC]

GHSV = 40k hr^{-1}
<λ> = 0.996
f = n/a
A = 0



[with O_2 modulation at 405 ºC]

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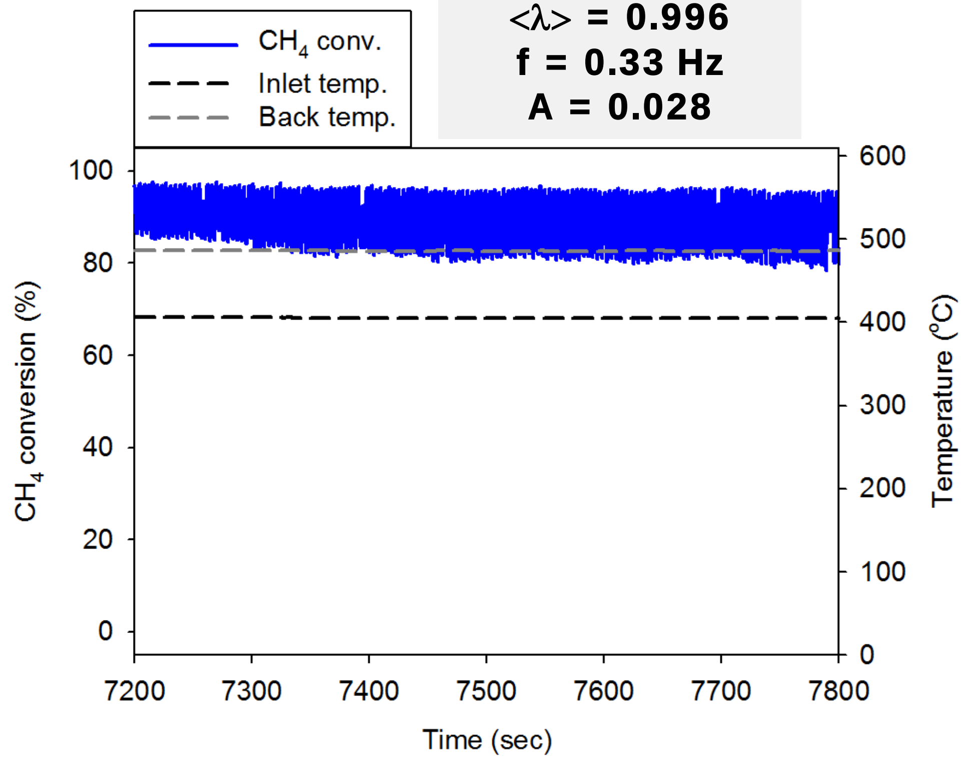

- *Modulation significantly enhances PGM + $Mn_{0.5}Fe_{2.5}O_4$ Spinel activity*

Baseline Catalyst Performance

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30 g PGM/ft³, 100 g Spinel/L

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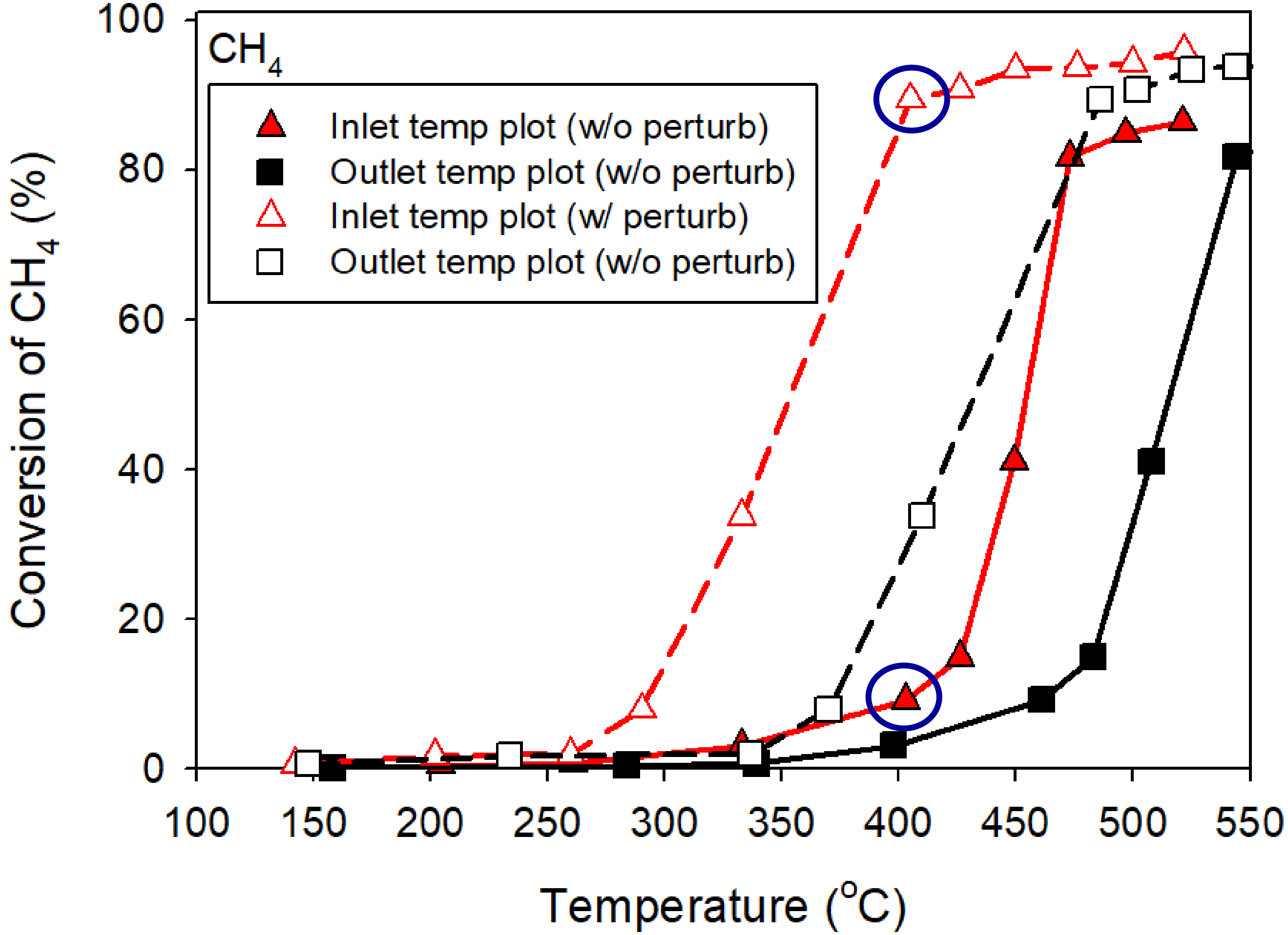

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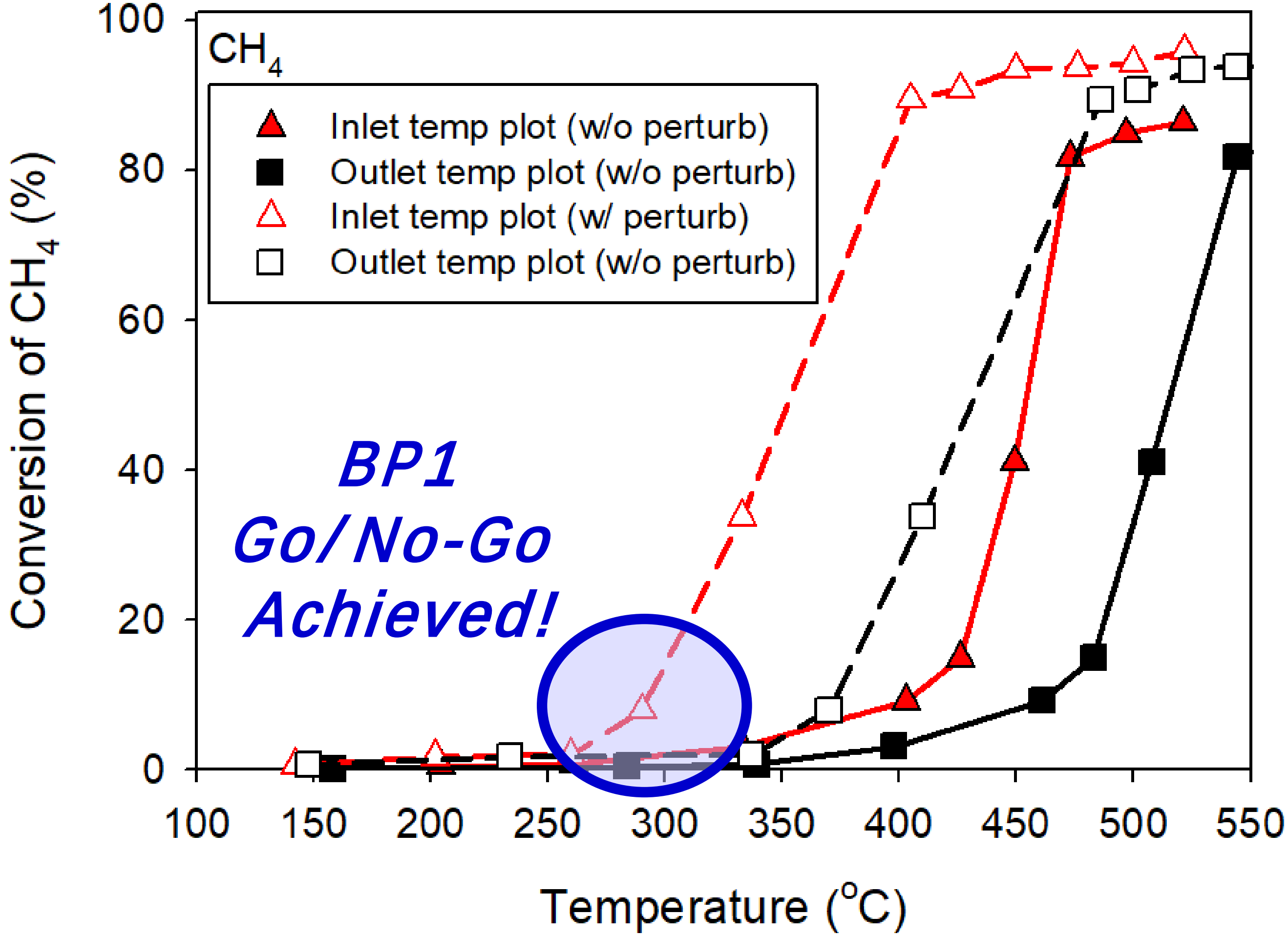
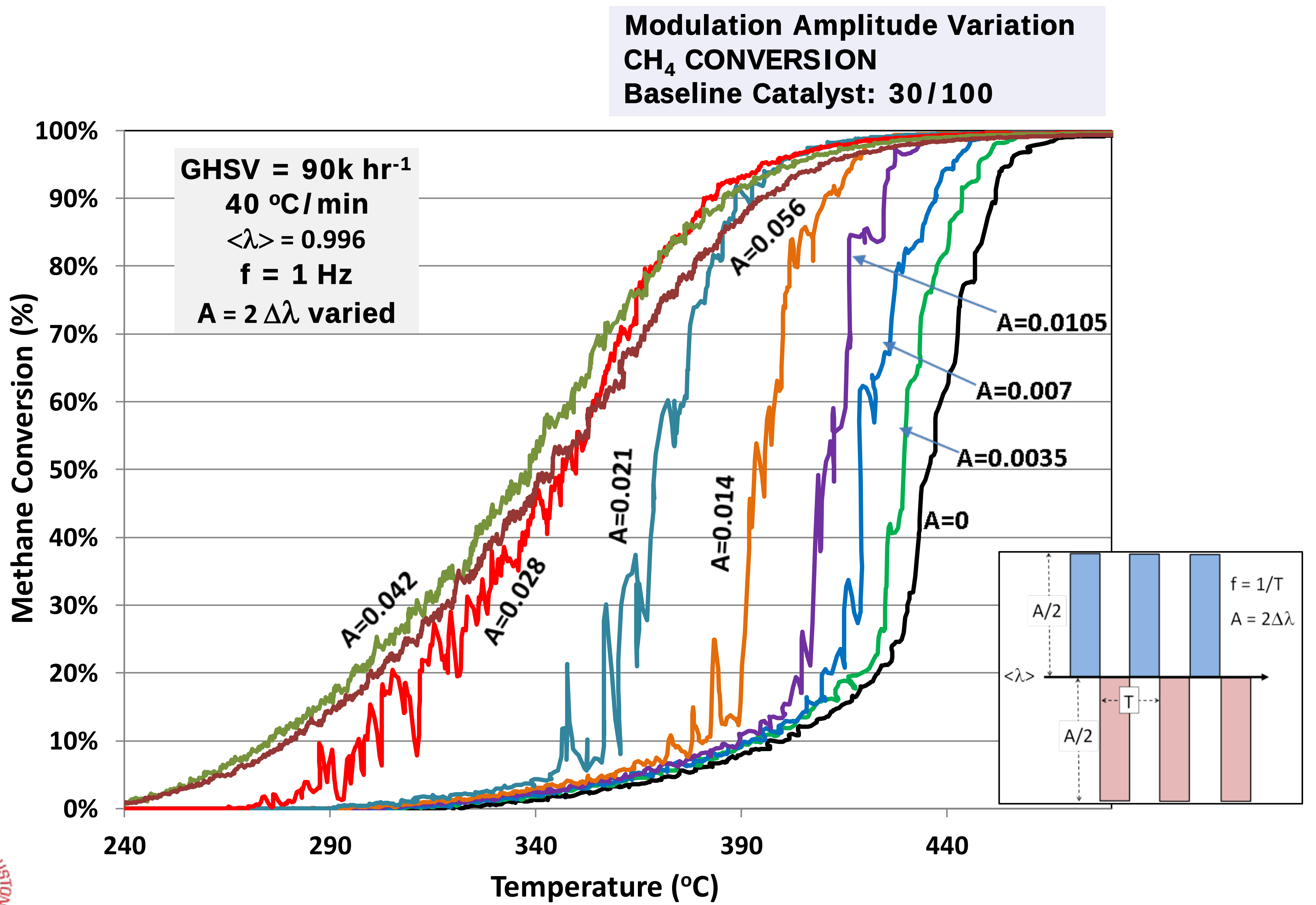


Impact of Modulation Amplitude



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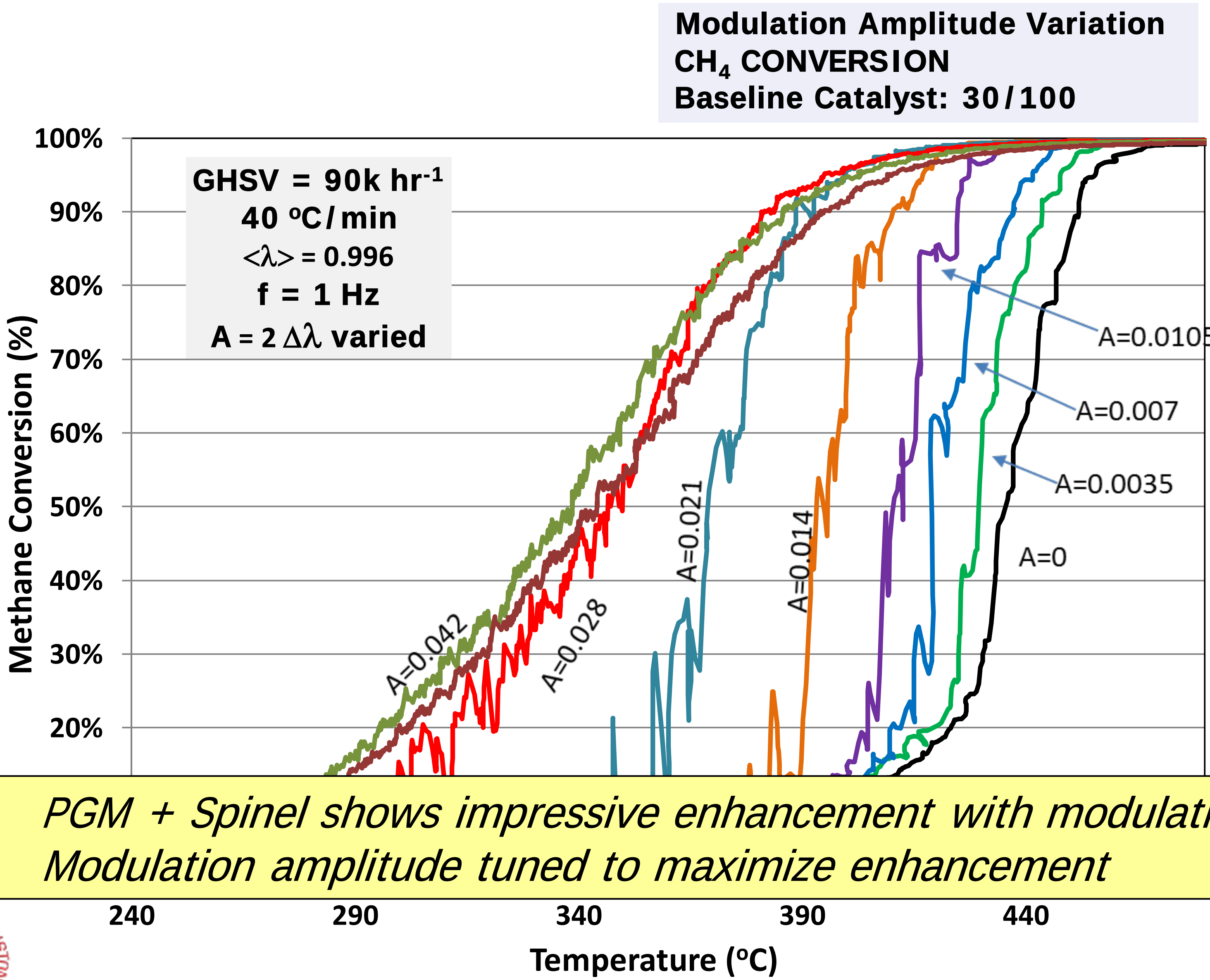
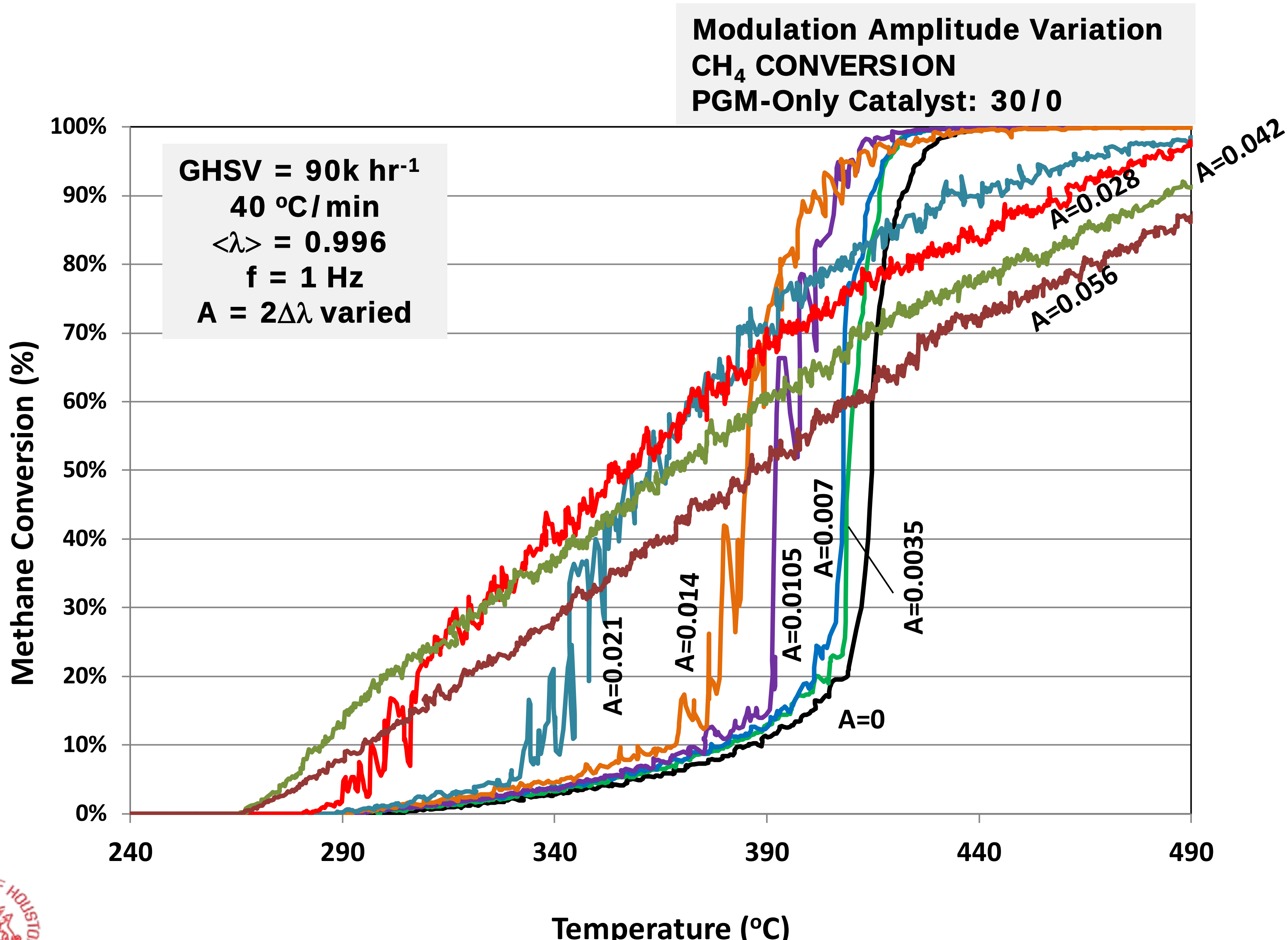
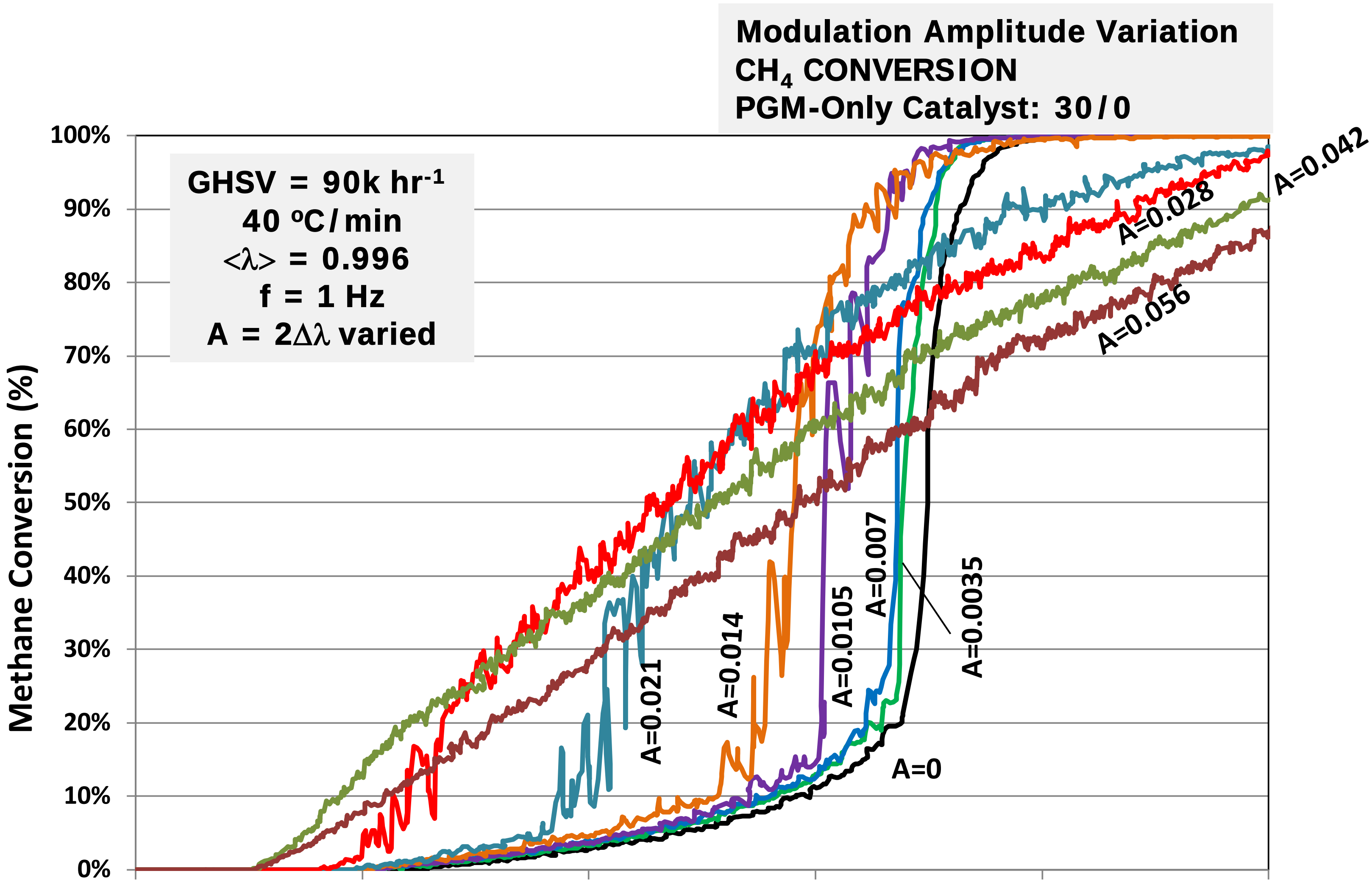


- *PGM + Spinel shows impressive enhancement with modulation*
- *Modulation amplitude tuned to maximize enhancement*

Impact of Spinel



Impact of Spinel

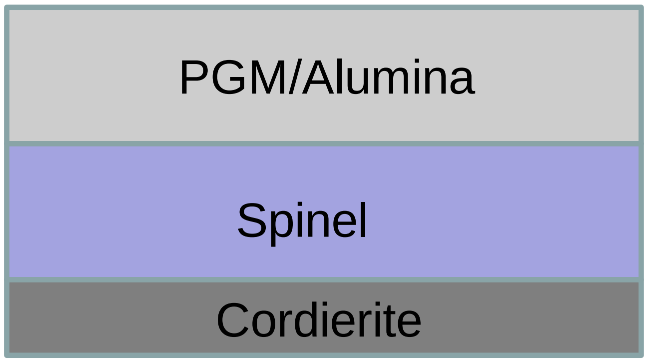


- *PGM w/o Spinel shows detrimental effect of modulation*
- *Spinel is essential ingredient to achieve low light temperature*

Spinel + PGM Coupling: Layered vs. Mixed Washcoat

PGM (30 g/ft³) + Spinel Dual-Layer

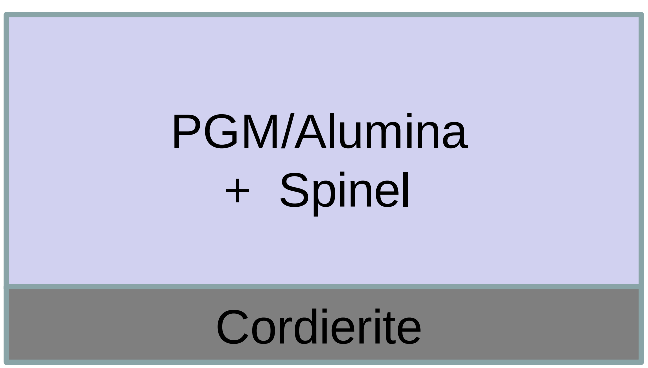
30/100 PGM/Spinel



Top layer (100 g/L; 1.63 g/in³)

Bottom layer (100 g/L; 1.63 g/in³)

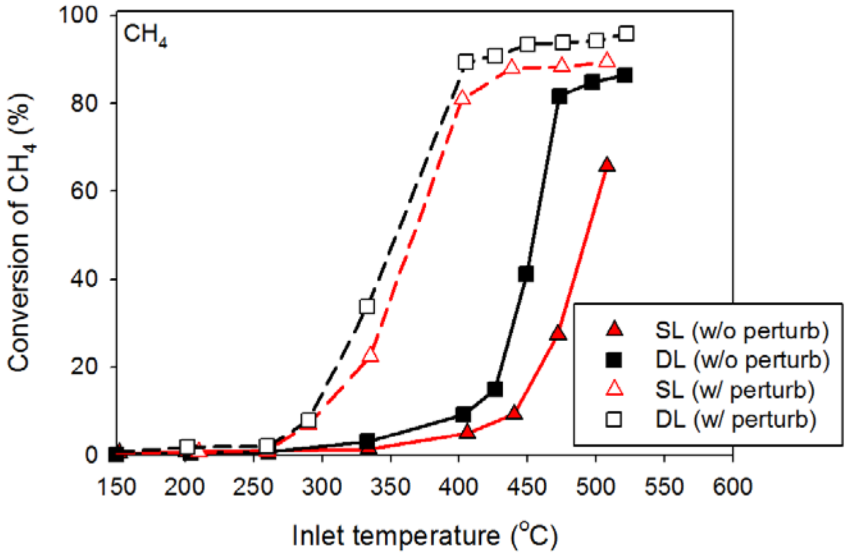
PGM (30 g/ft³) + Spinel Mixed Layer

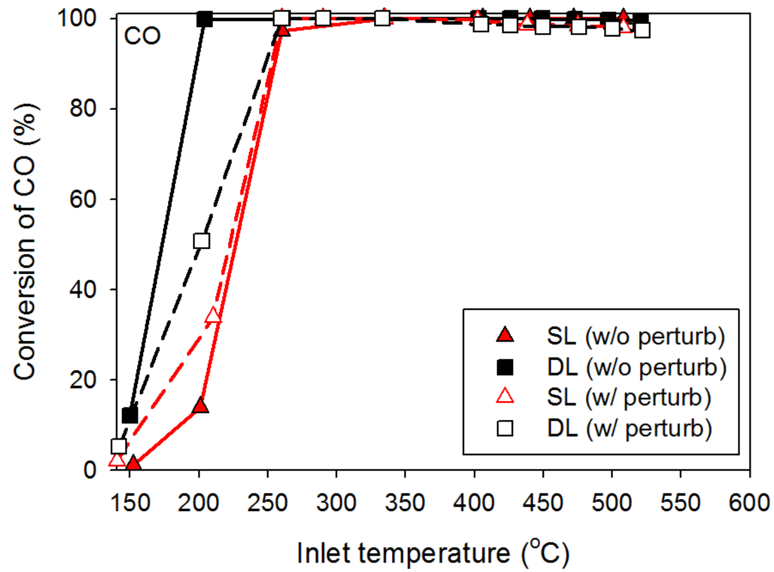


Total: 200 g/L (3.26 g/in³)

Impact of PGM & Spinel Proximity

Comparison: Single-layer (SL) vs. Double-layer (DL) 30/100 Catalysts





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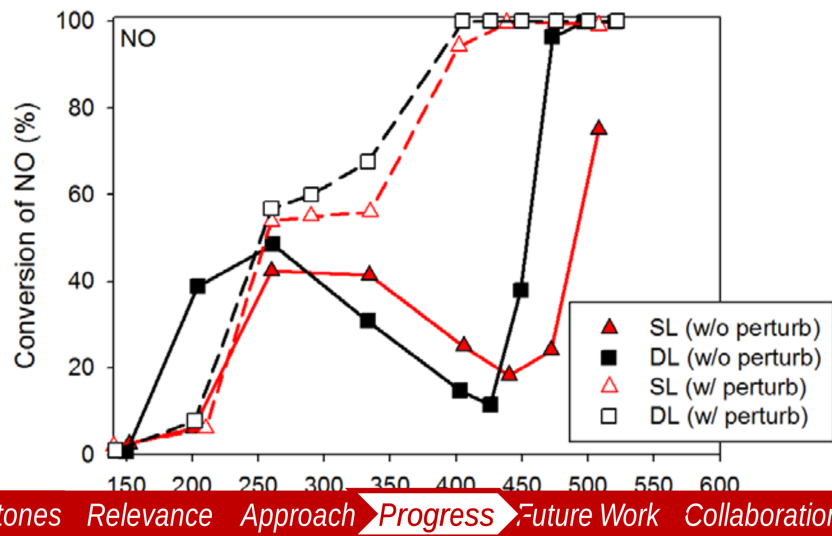

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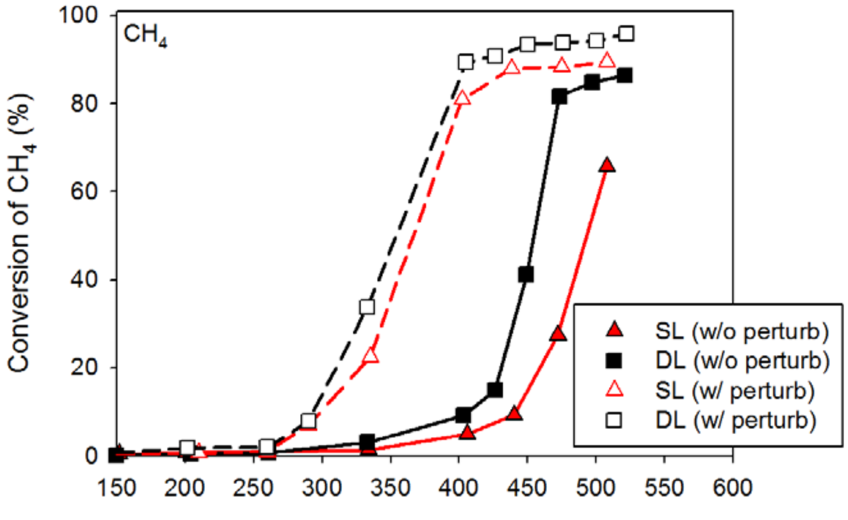

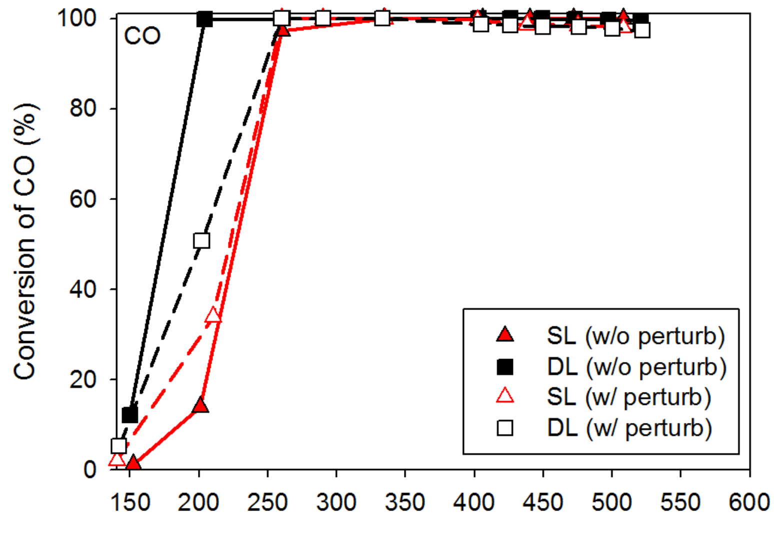

- *Dual-layer and Single-layer PGM + Spinel show similar results*
- *Close proximity of PGM & Spinel not essential*

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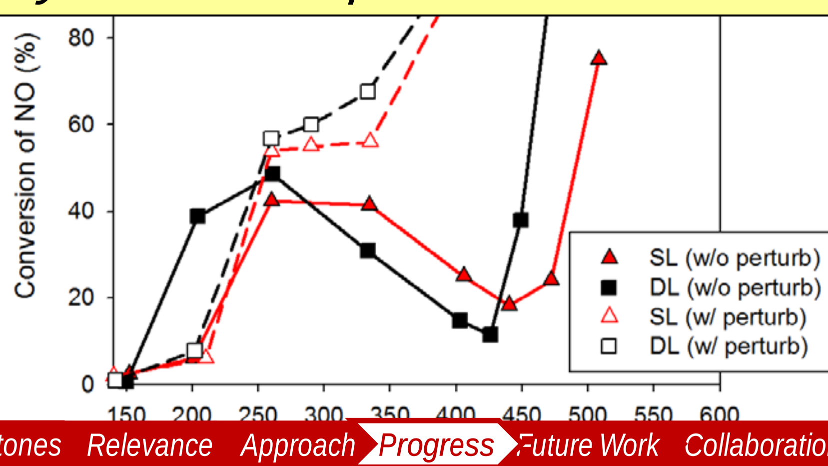


Conversion Enhancement: Observations

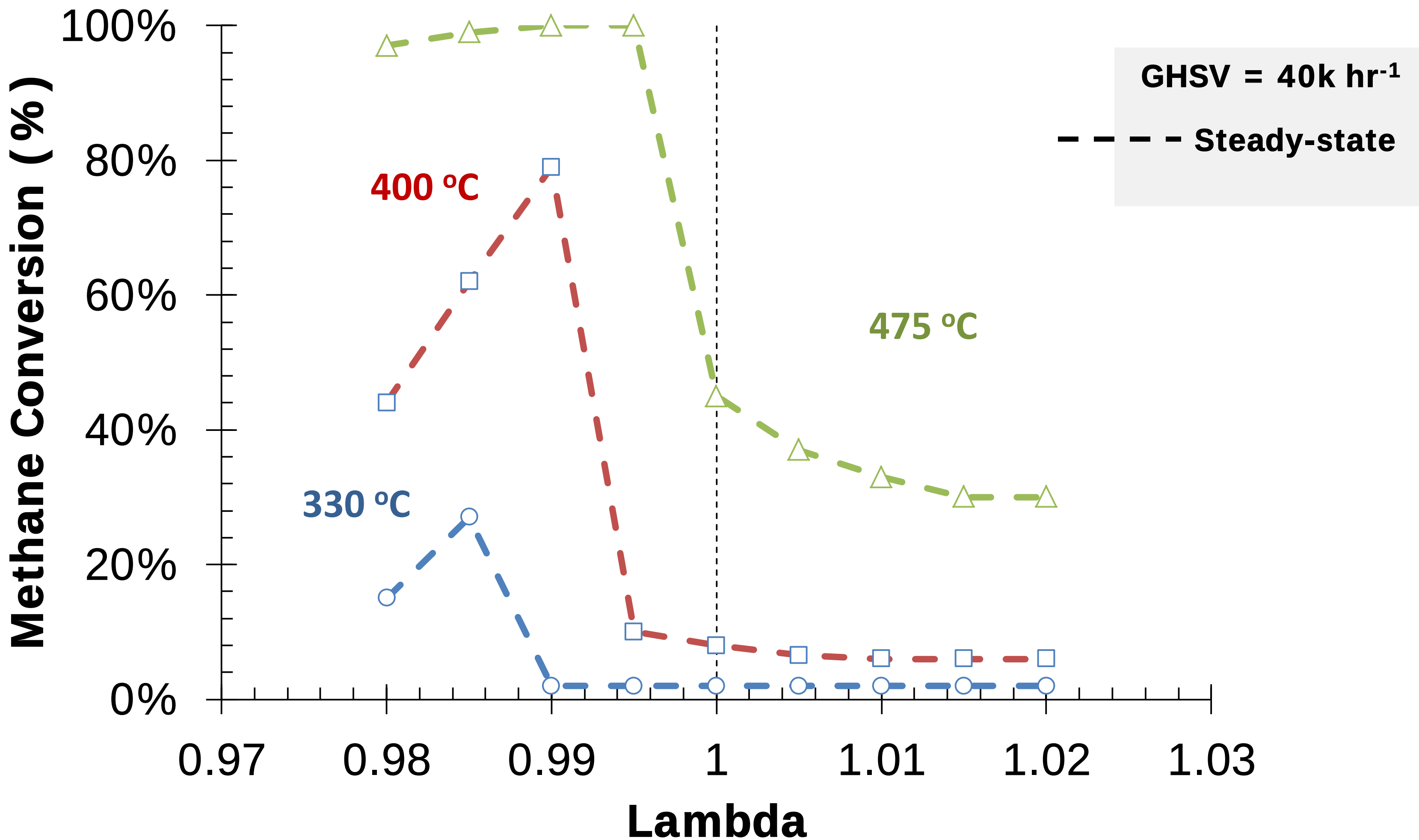
- PGM (at 30 g/ft^3) is much more active than Spinel (at ~100 g/L)
- PGM activity is enhanced by Spinel under modulation
- Modulation can be tuned to achieve maximum enhancement
- Mechanistic origin of enhancement related to strong dependence of methane activity on O_2 concentration:

Key may be Spinel oxygen storage & release keeps PGM in the more active mixed metallic-oxide state

Lambda Sweep: Methane Conversion

PGM-only Catalyst (30 g/ft^3; 60 g/L PGM)

L_I = 0 g/L



- *Strong O_2 inhibition as $\lambda \rightarrow 1$*

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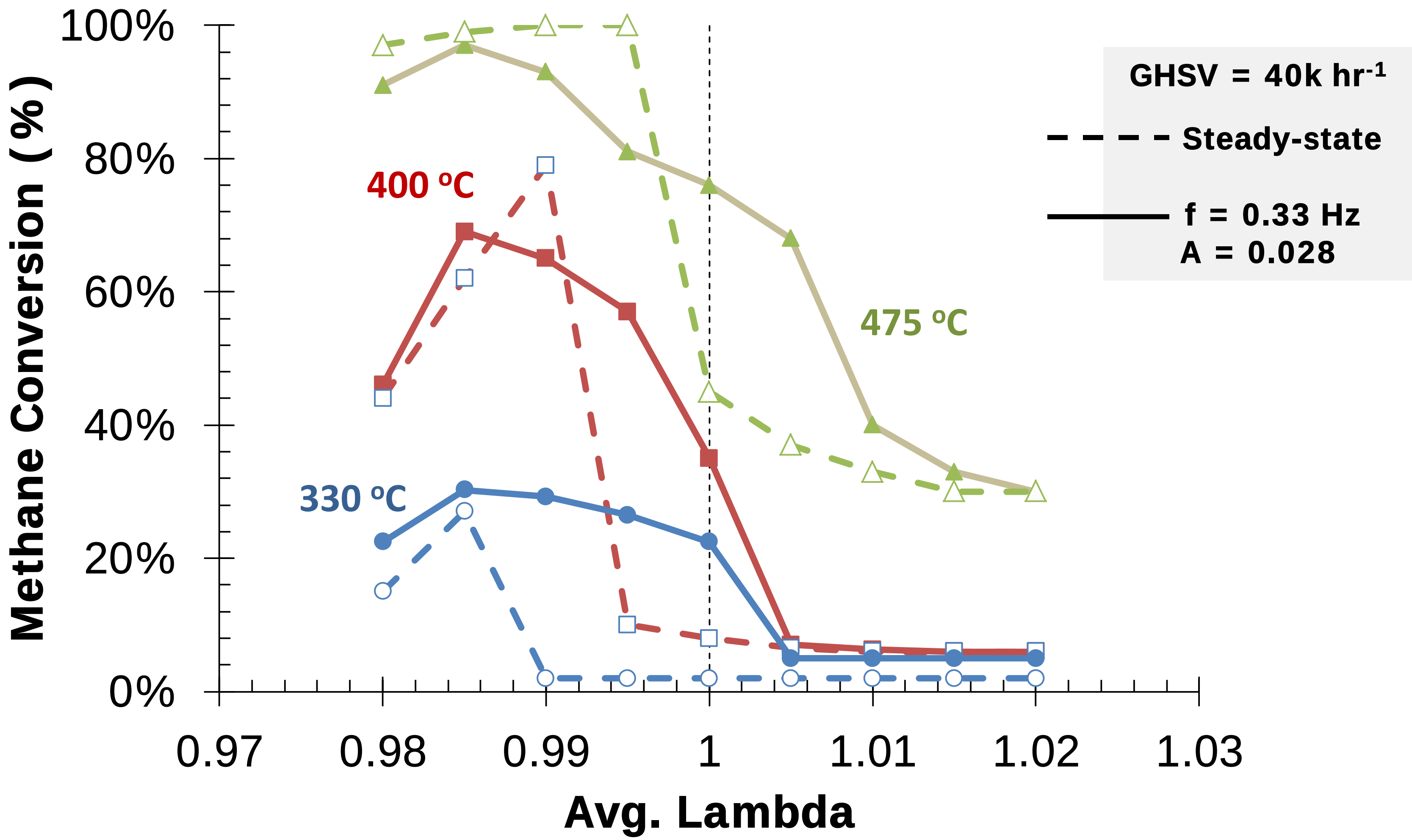

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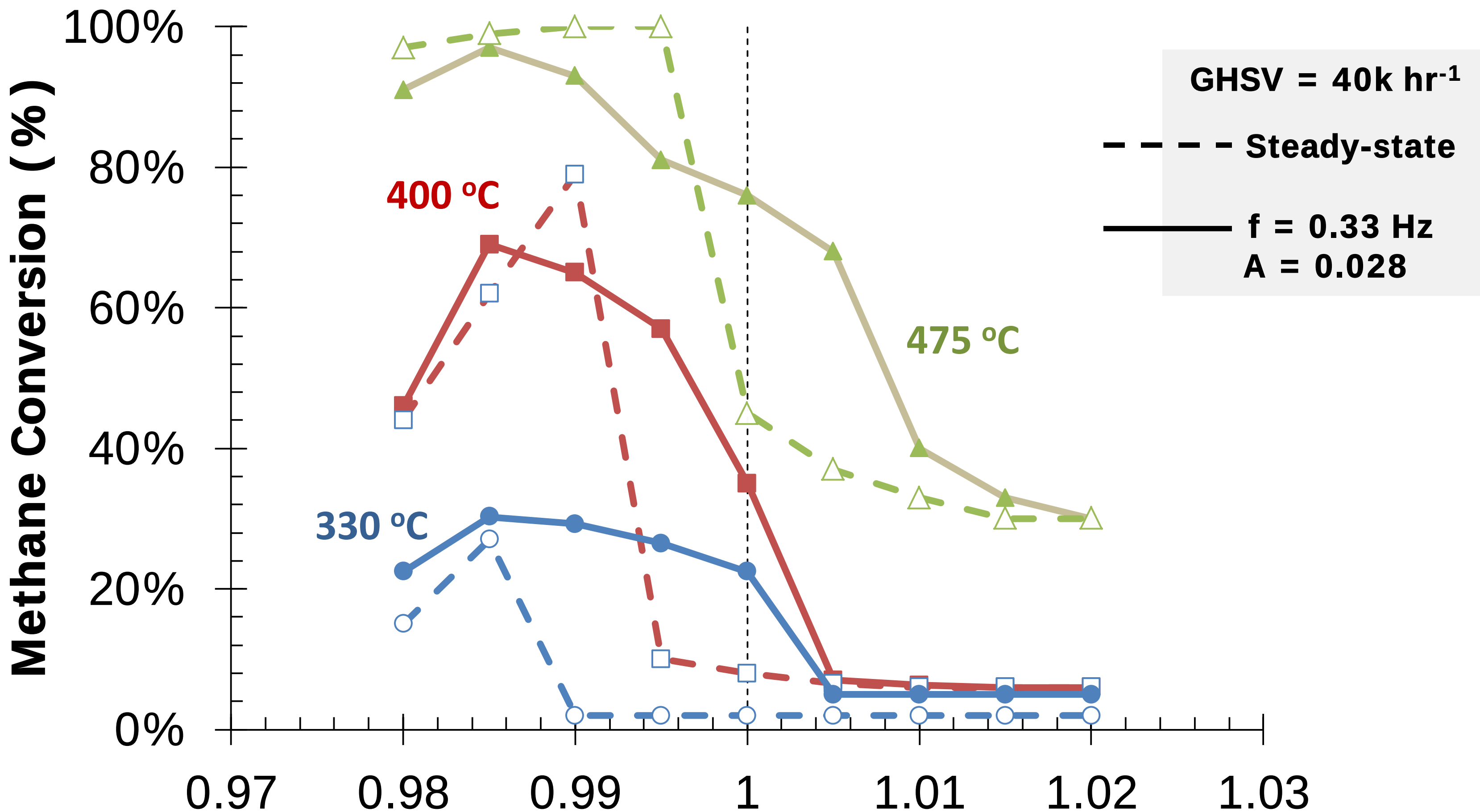
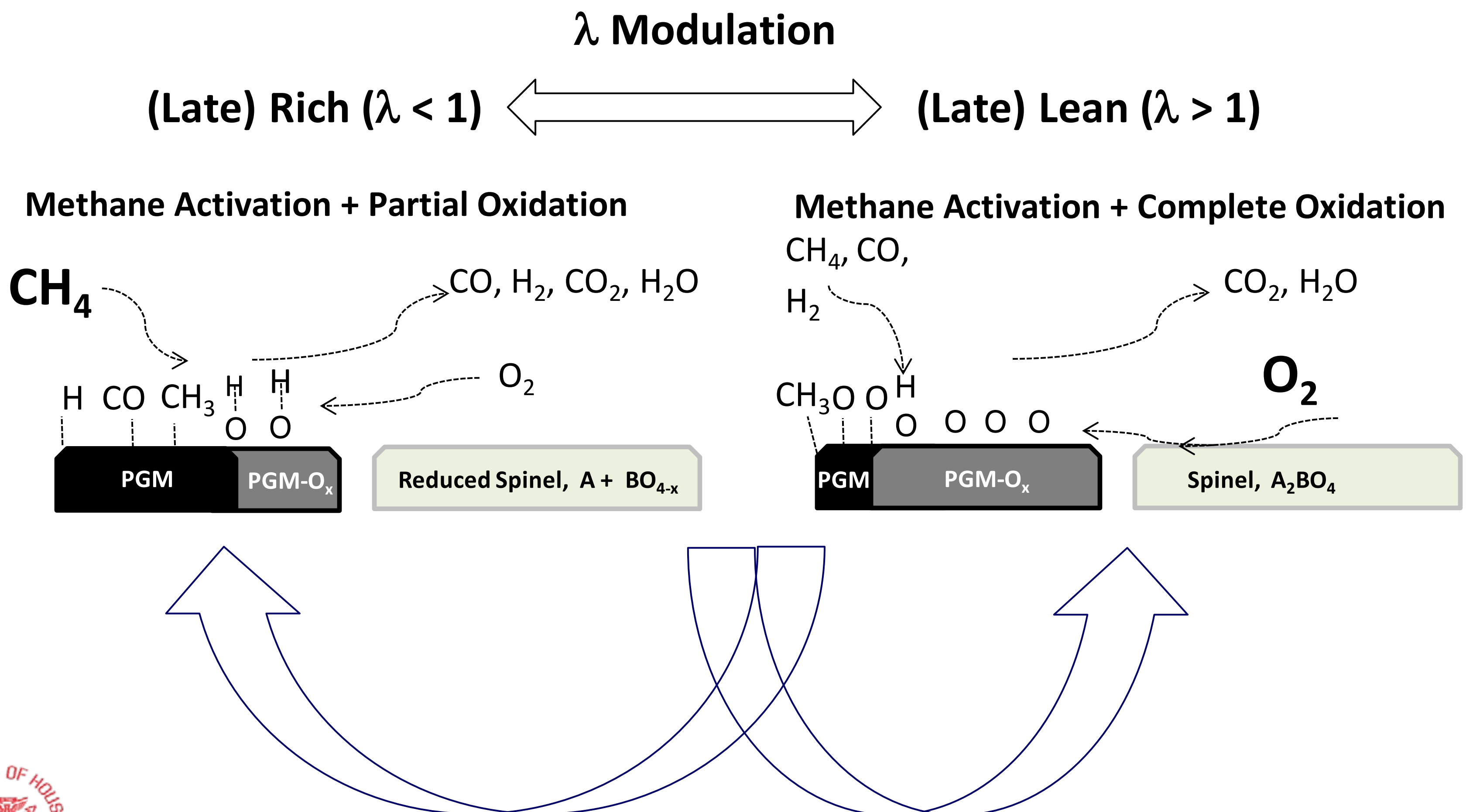


- *Strong O_2 inhibition as $\lambda \rightarrow 1$*
- *Modulation enhancement for PGM only catalyst*

Conversion Enhancement: Proposed Mechanism



Remaining Challenges & Barriers

- Lower light-off below 300 ^{o}C with PGM < 30 g/ft^3
- Understand mechanism for Spinel enhancement
  - Direct (methane oxidation) and/or Indirect (oxygen storage/release)
- Increase Spinel methane oxidation activity & dynamic oxygen storage capacity
- Understand spatial trends during modulation
- Develop predictive model to guide improvements
- Address sulfur tolerance and mitigation

Proposed Future Work

Task 2.1 – Discover new Spinel materials using computational screening.

- Descriptor-based DFT will be accelerated in order for the computations to drive synthesis efforts. Rank-ordering of Spinel compositions is goal.

Task 2.2 – Synthesize, characterize and screen candidate Spinel materials.

- Effort will continue based on experimental screening of Spinel powders with guidance from the computational efforts.

Task 2.3 – Develop mechanistic kinetic models of FWC materials.

- Kinetic modeling will continue for the Baseline and Reference materials, then move to the more active Spinel materials. Will involve conventional kinetics measurements, oxygen uptake and release kinetics, and Temporal Analysis of Products (TAP) experiments.

Proposed Future Work

Task 2.4 – Carry out flow reactor parametric studies of FWC materials.

- Focus on new FWC materials with Baseline and Reference materials complete.

Task 2.5 – Carry out spatially-resolved flow reactor studies of Baseline FWC materials.

- Spatially-resolved measurements of the Baseline and Reference material will be conducted to provide data for modeling efforts.

Task 2.6 – Perform stoichiometry modulation studies of FWC materials.

- Attention will be placed on new materials.

Proposed Future Work

Task 2.7 – Evaluate sulfur exposure on Baseline and new FWC materials.

- Comprehensive study of sulfur exposure will be conducted during this period to identify sulfur-tolerant materials.

Task 2.8 – Carry out modeling of monolith reactors containing Baseline Spinel materials.

- This is a key task for BP2 to set the stage for model-directed optimization later in the project.

Task 2.9 – Identify the best catalytic materials.

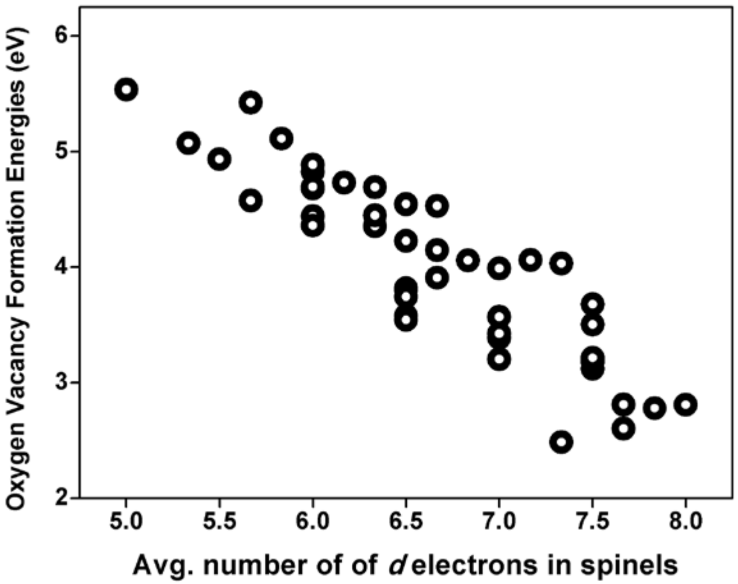
- This task spans all other tasks with convergence to the most active catalyst formulation the end goal.

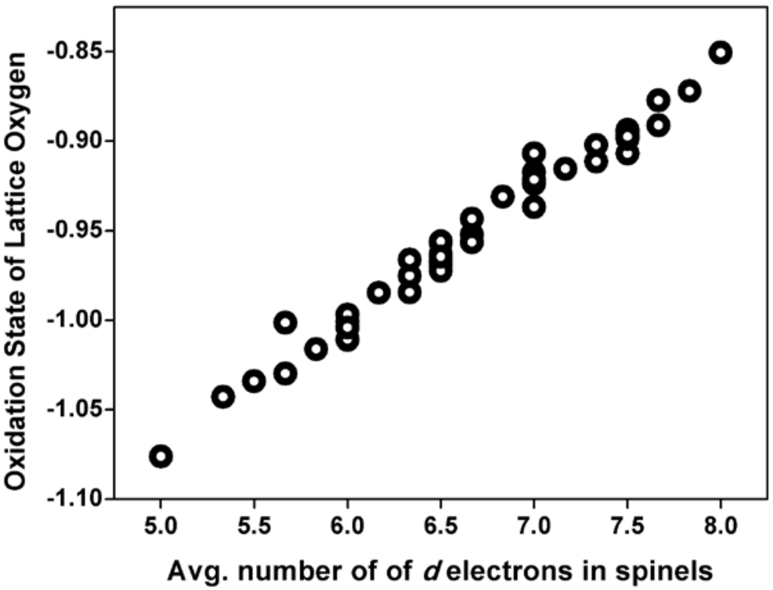
Summary

- **Relevance**
  - Enabling emergence of natural gas vehicles by removing emissions hurdle
- **Approach**
  - From molecular-level discovery & mechanism to development & demonstration
- **Technical Accomplishments & Progress**
  - Good progress on all fronts; BP1 milestones achieved
  - PGM + Spinel initial results encouraging; even better materials targeted
- **Collaborations & Coordination**
  - Cooperation: universities (UH+UVA), national lab (ORNL), industry (CDTi)
- **Proposed Future Research**
  - Converge on next-gen catalysts, integration, modeling, & optimization

Technical Backup Slides

d Electrons – a Key Intrinsic Property





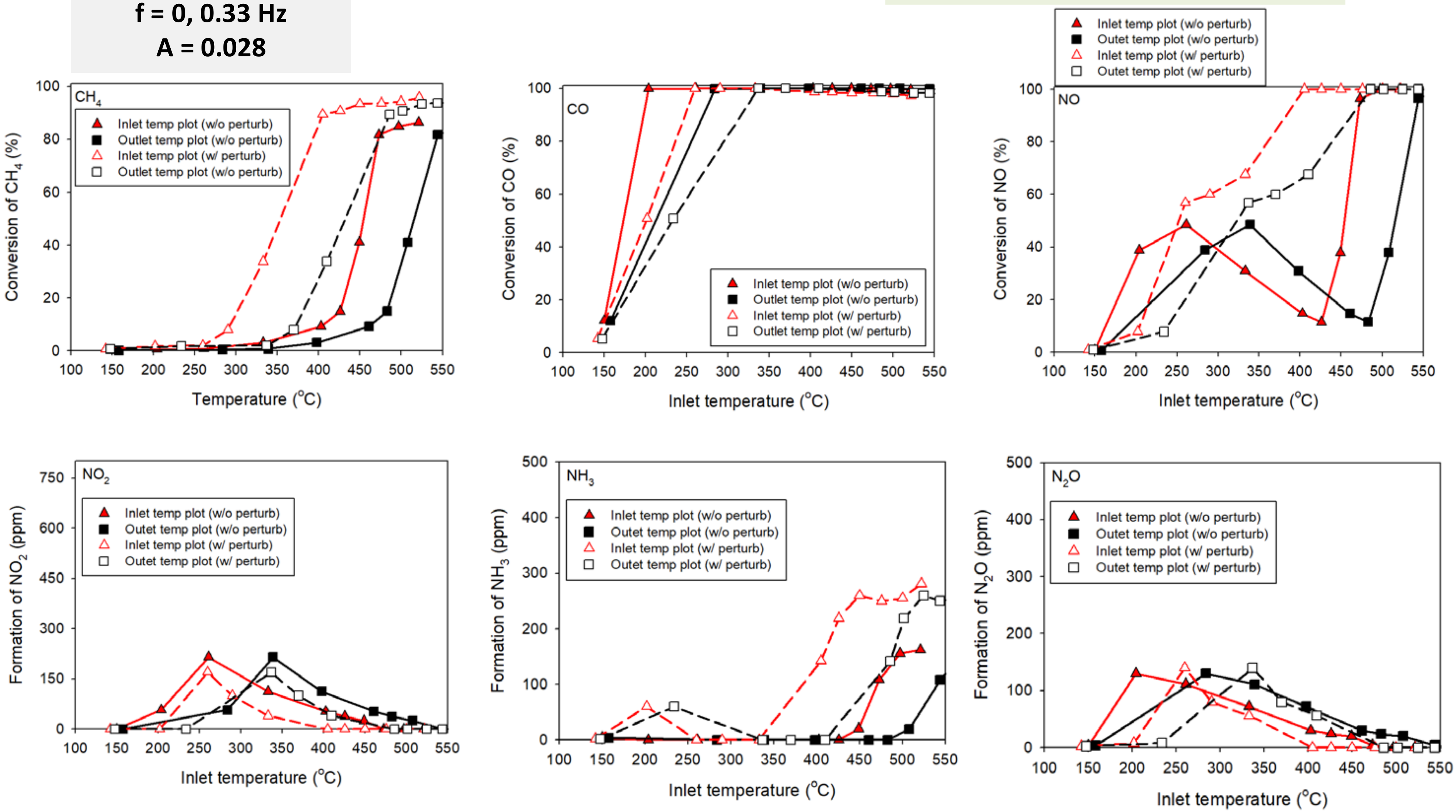
- Number of *d* electrons shows direct correlation to:
  - oxygen vacancy formation energy and
  - oxidation state of the lattice oxygens

- This allows for prediction of desired materials without rigorous DFT calculations

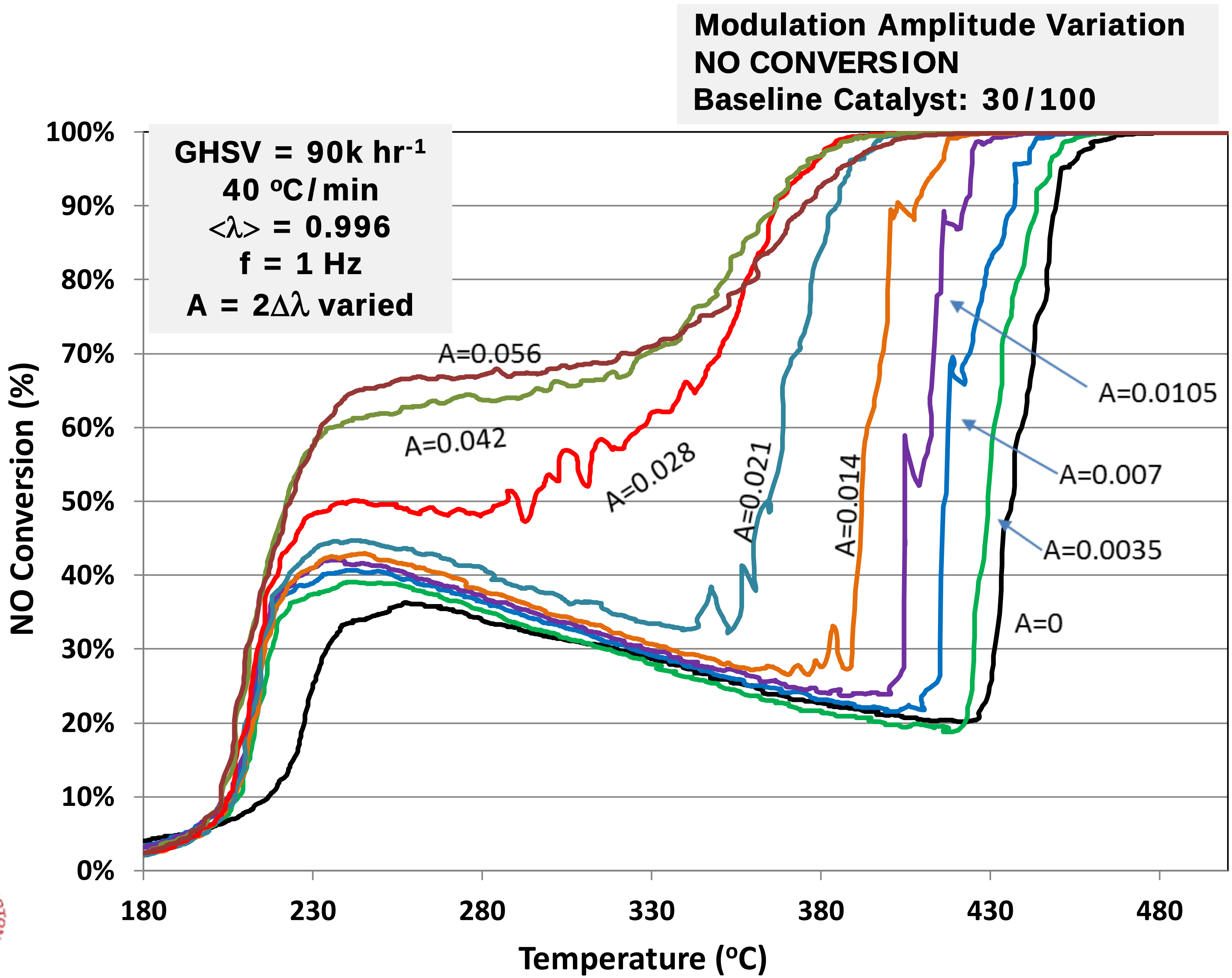
Baseline Catalyst Performance

GHSV = 40k hr^-1^
<λ> = 0.996
f = 0, 0.33 Hz
A = 0.028

Baseline (CDTi) 30/100

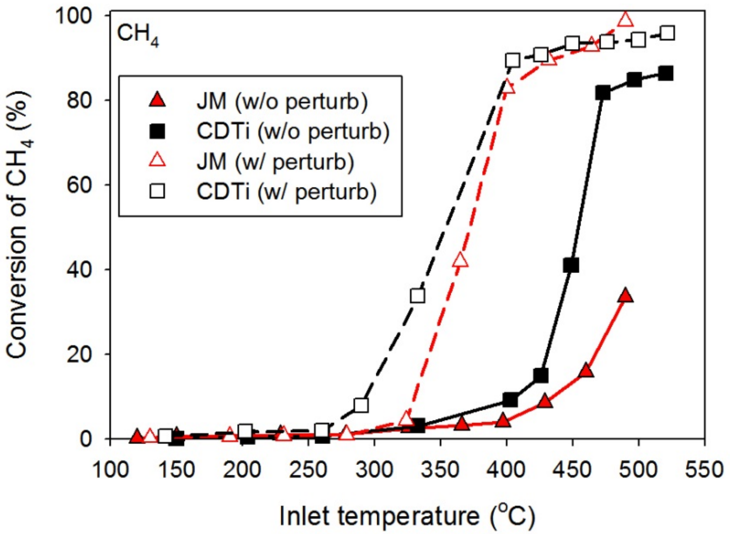


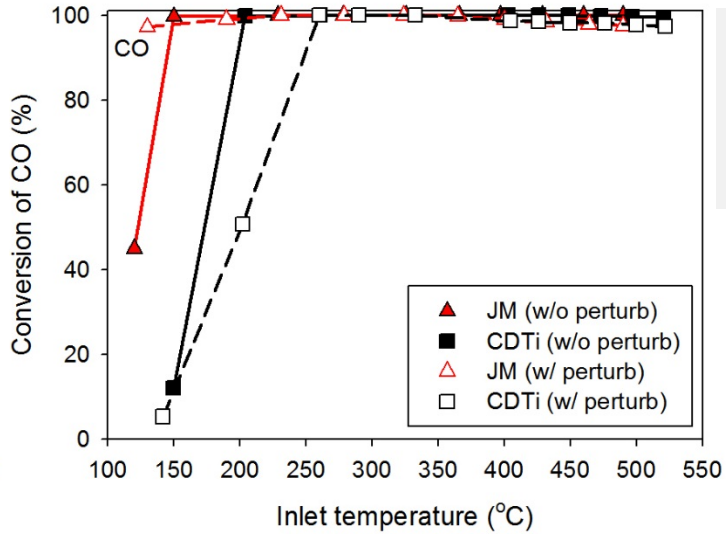
Impact of Modulation: NO Conversion



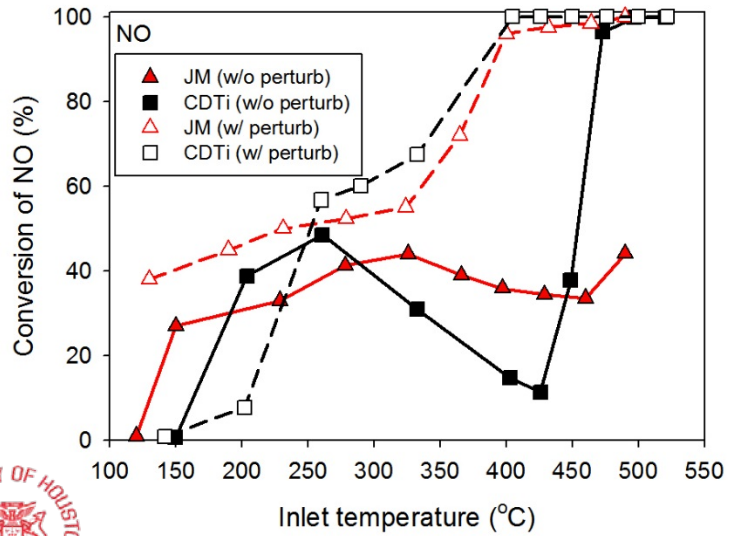
Catalyst Benchmarking

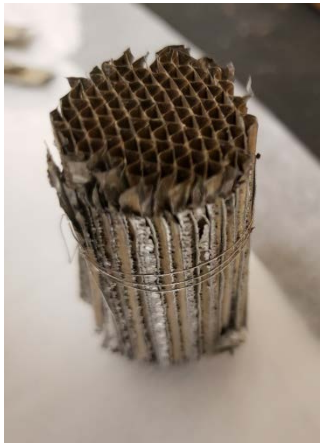
Comparison: **Reference (JM)** vs. **Baseline (CDTi) 30/100**



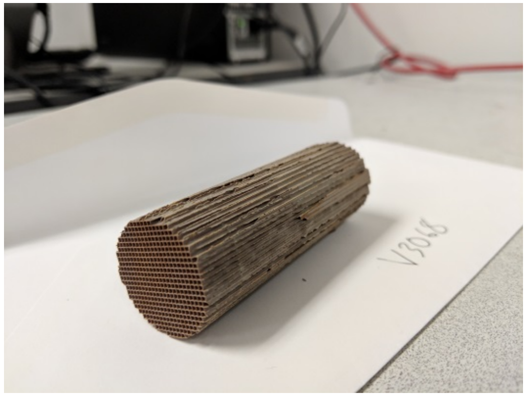


GHSV = 40k hr^{-1}
$\langle\lambda\rangle$ = 0.996
f = 0, 0.33 Hz
A = 0, 0.028



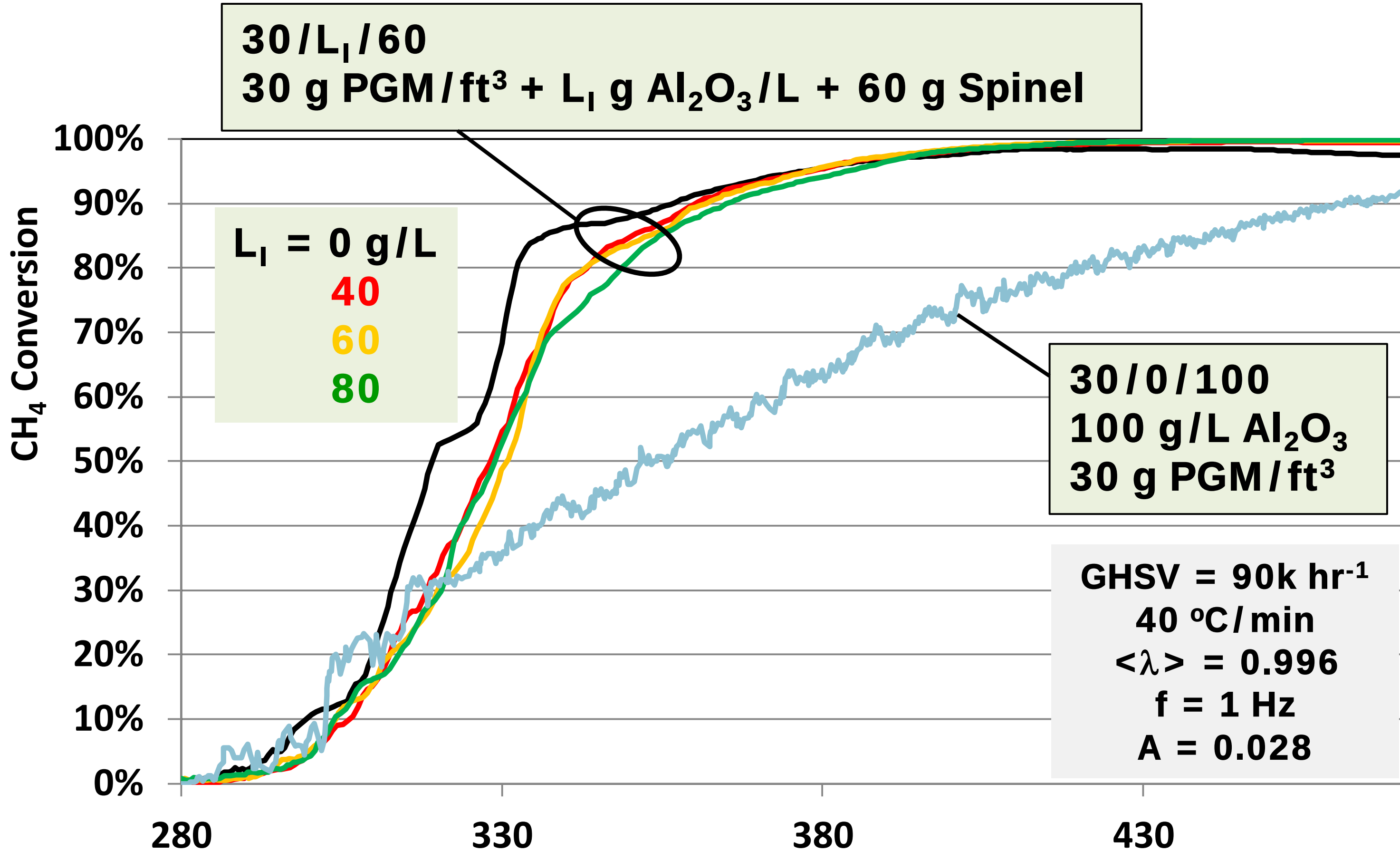


PGM / CeO_2 / Al_2O_3 (JM)



PGM / Spinel / Al_2O_3 (CDTi)
30 g {Pt(95%)+Pd(5%)} / ft^3

Impact of Intermediate Layer



- *Intermediate layer does not have significant impact*
- *Spinel required to give enhanced activity*